



AIAA 2001-3281
Methodology for Evaluating Raw
Material Changes to RSRM Elastomeric
Insulation Materials

S. Mildenhall
Thiokol Propulsion
Brigham City, UT

**37th AIAA/ASME/SAE/ASEE Joint
Propulsion Conference and Exhibit**

8-11 July 2001
Salt Lake City, Utah

METHODOLOGY FOR EVALUATING RAW MATERIAL CHANGES TO RSRM ELASTOMERIC INSULATION MATERIALS

Scott D. Mildenhall
Senior Principle Engineer
Thiokol Propulsion
Brigham City, UT

Abstract

The Reusable Solid Rocket Motor (RSRM) uses asbestos and silicon dioxide filled acrylonitrile butadiene rubber (AS-NBR) as the primary internal insulation to protect the case from heat. During the course of the RSRM Program, several changes have been made to the raw materials and processing of the AS-NBR elastomeric insulation material. These changes have been primarily caused by raw materials becoming obsolete. In addition, some process changes have been implemented that were deemed necessary to improve the quality and consistency of the AS-NBR insulation material. Each change has been evaluated using unique test efforts customized to determine the potential impacts of the specific raw material or process change. Following the evaluations, the various raw material and process changes were successfully implemented with no detectable effect on the performance of the AS-NBR insulation. This paper will discuss some of the raw material and process changes evaluated, the methodology used in designing the unique test plans, and the general evaluation results. A summary of the change history of RSRM AS-NBR internal insulation is also presented.

Introduction

The space shuttle reusable solid rocket motor (RSRM) program faces many material change and obsolescence issues. Because the RSRM is part of the manned space flight shuttle system, these changes typically require extensive side-by-side testing and verification prior to implementation. It is critical that the erosion, structural, bonding, and processing characteristics of the elastomeric insulation materials be maintained.

Obsolescence issues are caused by any of several factors including, discontinued products due to poor sales, changing environmental regulations,

manufacturers going out of business or being bought-out, or the need for new manufacturing equipment or facilities. Usually the amount of an elastomeric raw material used on the RSRM is comparatively small and efforts to influence a manufacturer to not make a change are futile.

Changes to elastomeric insulation raw materials have proven to be inevitable and repeating. Changes have affected each of the Reusable Solid Rocket Motor (RSRM) elastomeric insulation materials. This document focuses on the changes that have been made to the primary RSRM internal insulation material, asbestos and silicon dioxide filled acrylonitrile butadiene rubber (AS-NBR). These changes range from simply upgrading a raw material manufacturer's production line to completely changing from an obsolete raw material to a new, chemically different, replacement raw material. Typically when an obsolescence issue is identified, a reserve or stockpile of the raw material is purchased to ensure adequate time to identify and evaluate a replacement. However, due to the obsolescent nature of some of these changes, frequently little time is available to evaluate the change.

AS-NBR insulation is ordered from one qualified manufacturer that has supplied this material throughout the shuttle solid rocket motor program. The long-term working relationship established between this supplier and Thiokol has greatly enhanced the ability to communicate and evaluate raw material change issues. AS-NBR insulation is mixed in a Banbury® type internal mixer, and calendered into sheet stock. Extruded AS-NBR parts are also made for regions of the RSRM that require unique pre-formed configurations.

AS-NBR is the primary internal insulation material in the RSRM, and is also used to fabricate the igniter insulation and nozzle flexible boot. The ID surfaces of RSRM case segments are coated with Chemlok®

vulcanization adhesives. Green or uncured AS-NBR insulation is laid against these adhesive coated surfaces using multiple layers of sheet stock until the desired thickness is attained. AS-NBR extrusions are also installed in some regions of the segments. The insulation lay-up is covered with a release cloth, breather cloth material, and a vacuum bag. The segments are cured under vacuum in a large autoclave at 100 psi and temperature of 290 °F. Embedded thermocouples are monitored to ensure that the

insulation materials reach a desire temperature-time profile before completing the cure cycle.

Summary of Changes to AS-NBR Insulation

The following table lists the changes that have occurred to AS-NBR internal insulation. An approximate date is listed for each change to establish the chronological order of the changes. Selected changes will be discussed in further detail.

Summary of Changes to AS-NBR Insulation		
Title of Change	Date	Description of Change
New Mixer	1980s	A new 500 lb capacity Banbury® type internal mixer was purchased by the AS-NBR manufacturer to replace the 400 lb capacity mixer as the primary mixer. The 400 lb mixer was retained as a backup mixer.
New Calender	1980s	A new calender was purchased by the AS-NBR manufacturer. The old calender was retained as a backup.
Altax® Accelerator	1987	The original manufacturer of Altax® accelerator discontinued making this accelerator. The distributor elected to continue to market Altax® accelerator under the same brand name, but from a different manufacturer.
Kadox® 930C Zinc Oxide	1993	Kadox® 930C zinc oxide was selected to replace Protox® 166 zinc oxide, which was discontinued.
Agerite Stalite S® Antioxidant	1993	Agerite Stalite S® was selected to replace Agerite White®, which was discontinued.
HiSil® 233 Silicon Dioxide	1993	The alkali source used in the manufacture of silica was changed from caustic soda to soda ash.
	1994	Due to environmental concerns associated with the use of soda ash, the silica manufacturer changed the alkali source from soda ash to caustic soda.
	1996	The silica manufacturer constructed a second sodium silicate furnace. The new furnace uses soda ash as the alkali source. The old furnace was still using caustic soda as its alkali source. Silica from both furnaces could be blended.
Harwick® F-1500 Stearic Acid	1997	Harwick® F-1500 stearic acid was selected to replace Hydrofol® 1800B stearic acid, which was discontinued.
Picco® 6100 Resin Tackifier	1997	A new manufacturing line was built for the production of Picco® 6100 resin, which is used to increase the build tack of the uncured AS-NBR insulation.
Sulfur Oil	1999	The sulfur manufacturer approved a new oil source. Oil is added to the powdered sulfur to prevent dust hazards, and to enhance dispersion during mixing.
Sulfur Masterbatch Refining	1999	A refining step was added to the fabrication process of the sulfur masterbatch to eliminate sulfur clumps.
Sulfur Masterbatch Crossblending	2000	Three 50-pound sulfur masterbatches are crossblended to improve the overall uniformity of the masterbatch and to reduce the cost of analysis of the masterbatches. Previously each 50-pound sulfur masterbatch was processes and tested separately.

The AS-NBR manufacturer has submitted other change notifications indicating a change in the manufacturer of a raw material. These are frequently determined to be only a change in ownership of a company or ownership of a production facility and not true changes to the raw material. In order to better understand and control these types of changes, the AS-NBR manufacturer currently documents (on their raw material specifications) the supplier and the location where the raw materials are manufactured. The AS-NBR supplier purchases many raw ingredients from major rubber chemical suppliers (or distributors); only a few raw materials are bought directly from the manufacturer. Documentation of the location of manufacturing is also required on raw material supplier certifications. This documentation change was implemented after a raw material supplier sent sulfur that was manufactured at a different location. The new sulfur, which met the sulfur supplier's specification, resulted in clumping of the sulfur during a masterbatch mixing operation. The sulfur clumps did not disperse during the subsequent mixing processes and resulted in small hard sulfur-rich black spots in the cured AS-NBR insulator.

Test Methods Used to Evaluate Raw Material Changes

The AS-NBR insulation specification requires that the following tests be conducted by the manufacturer on each lot of material as quality conformance inspection tests:

- Shore A hardness
- Tensile strength and elongation in the parallel and perpendicular-to-roll direction or predominant fiber direction ($//$, \perp)
- Specific gravity
- Mooney viscosity
- Initial scorch characteristics

Because of their importance in characterizing the physical properties of the insulation these tests are always run when evaluating raw material changes. These tests are also conducted on each production lot of AS-NBR; therefore a large production material database is available for comparison. This database is also used to trend the effects of changes following implementation.

The AS-NBR insulation specification identifies a set of qualification tests that are typically conducted to evaluate all raw material changes. Qualification tests include all of the quality conformance tests listed above plus the following:

- Specific heat
- Thermal conductivity

Qualification tests are used to evaluate changes, but may not be sufficient to fully characterize a specific change. The AS-NBR specification also allows for other additional tests as required to verify that the material is suitable for the end use. In most situations additional tests are added for a more complete change evaluation. These additional tests may include bond tests, sub-scale hot fire tests, accelerated aging bond tests, sub-scale hot fire tests, accelerated aging bond tests. Data for comparison for these additional tests may be limited, so a control test is typically run. Also lot-to-lot variation of quality conformance data requires the use of a control sample on evaluation tests. The control material is preferably mixed at the same time as the evaluation material using all of the same lots of raw materials, except for the raw material being changed. The control material is also used throughout the testing to help verify that specimen preparation and test procedures are properly conducted.

Material Samples Used in Raw Material Change Evaluations

Changes are typically evaluated first on the new and old raw materials, particularly if the replacement raw material is expected to be a drop-in replacement. This also depends on the tests that have been developed to characterize the particular raw material. These tests are usually very specific and based on the type, form, and function of the raw material.

The raw material change is then evaluated in the compounded or mixed AS-NBR material. Analytical scale-up of rubber mixing is difficult, so full-scale 500 pound batches at the manufacturer are typically used. Small-scale (6-10 pound) mixing has been used to assist in down-selecting new raw materials, but is always followed with full-scale processing.

AS-NBR insulation is mixed using a Banbury® type internal mixer. The AS-NBR material is calendered into sheet stock of 0.05, 0.10, 0.13, or 0.20 inch thickness. Five different extrusions are also made using sheet stock as the feed material. For most evaluation efforts 0.100-inch thick sheet stock is ordered. One configuration of extrusion may also be ordered if the change could affect the ability to extrude the AS-NBR material.

Raw Material Change Evaluation Methodology

Changes to insulation raw materials generally fall under one of the following categories:

- 1) A process or ingredient change to the raw material that is not expected to change the properties of the raw material
- 2) An obsolescence issue that causes the raw material to be replaced with a new raw material that is the same chemically and is expected to be a drop-in equivalent replacement
- 3) An obsolescence issue that causes the raw material to be replaced with a new raw material that is chemically different that may cause the insulation material to perform differently.

The category, as defined above, of a specific change will typically influence the number of lots of materials ordered to evaluate the change and the number of tests conducted. Other factors are considered when evaluating raw material changes. The intended function of the raw material being changed dictates which additional tests (other than the specification qualification tests) will be conducted to evaluate the change. AS-NBR raw materials fall under one of the following general classifications:

- Elastomer
- Filler
- Curative agent
- Cure accelerator
- Cure activator
- Antioxidant
- Tackifier
- Plasticizer

Changes to the elastomer package require physical property tests to verify polymer structure and strength and to verify that the cross-link density is comparable. Mooney viscosity testing characterizes the flow characteristics of the uncured insulation material. Initial scorch, and rheology tests are conducted to ensure that the elastomer and curative package are compatible and react at the desired rates and temperatures.

Changes to the fillers generally require structural testing. Viscosity tests are also conducted to ensure that the material has the desired degree of flow during the cure process. Insulation erosion testing is conducted to verify that the thermal and ablative characteristics have not changed.

A change to the curative agent, accelerator, or activator is cause to conduct initial scorch and rheology tests. Additional physical properties tests are conducted to verify that the cross-link density of the cured insulation has not changed significantly. Insulation erosion testing may also be conducted.

Antioxidant changes require aging tests to ensure that the insulation material is resilient to the effects of oxidation and ozone degradation. Bond tests, including aging, are required since many antioxidants migrate to the surface of the material and could affect the bond interface.

Tackifier changes require processing tests to verify that the material has adequate build tack. These tests can initially be conducted as bench top tests, but are usually followed by a full-scale process simulation article.

Plasticizer changes are evaluated using comparative sub-scale and full-scale mix testing. Mix temperatures, mix times, and mechanical loading on the mixer are observed. Mechanical properties are also measured to determine the effects of the plasticizer on the cured insulation.

Discussion of AS-NBR Raw Material Changes

Descriptions of selected changes to RSRM AS-NBR insulation raw materials are documented in the remainder of this report. The changes that are discussed are those that have occurred most recently (since 1987).

Altax® Accelerator

Altax® (benzothiazyl disulfide), an accelerator used in AS-NBR insulation, was manufactured domestically for 60 years. The original manufacturer decided to discontinue production of this and other accelerators. The distributor who marketed these products elected to continue to supply the material, but from a new manufacturer. The new material used the same Altax® brand name and specification.¹

Samples of the old and new Altax® were obtained along with the supplier's test data for each sample. Melting point, moisture content, and ash content tests were repeated at Thiokol. The results indicated that all parameters met specification except melting point.² These results were communicated to the supplier who acknowledged the shift in melt temperature and indicated that the Altax® specification would be

modified to list a higher melt point. The high melt point was caused by a slightly higher purity level. This was not expected to have any significant effect on the performance of the Altax®.

Two small-scale batches of a model test formula were mixed using old and new Altax®. This model formula was very similar to the AS-NBR formula, except additional silica was substituted for the asbestos fibers. These batches were compared using the following tests:

- Shore A hardness
- Tensile strength and elongation
- Specific gravity
- Mooney viscosity
- Initial scorch
- Rheology
- Tear strength

No significant differences were observed between the old and new Altax® batches. A full-scale production batch was then produced by the AS-NBR supplier using new Altax®. The following specification tests were conducted:

- Shore A hardness
- Tensile strength and elongation (//, ⊥)
- Specific gravity
- Specific heat
- Thermal conductivity
- Mooney viscosity
- Initial scorch

The following additional material properties were also tested:

- Tear strength (//, ⊥)
- Ash content
- Shrinkage
- AS-NBR / liner bond tests
 - 0 & 7 week aging at 77 °F and 150 °F
- 180° peel
- Tensile adhesion
- Lap shear
- AS-NBR /AS-NBR T-peel
- 180° peel - AS-NBR /metal
- Tensile adhesion - AS-NBR /metal
 - 0, 2, 4, 6, weeks aging at 75 °F and 135 °F
- Thermogravimetric analysis

No significant differences were observed in AS-NBR batches mixed with the new Altax® when compared with AS-NBR mixed with old Altax®.

Kadox® 930C Zinc Oxide

Protox®166, an American Process grade zinc oxide, was replaced by Kadox® 930C French Process grade zinc oxide. The notification that manufacture of Protox®166 had been discontinued was received from the zinc oxide manufacturer in October 1989. The zinc manufacturer recommended Kadox® 930C zinc oxide as the replacement for Protox®-166 zinc oxide, stating that particle size and treatment levels (surface coating) of both products were essentially the same and that they would perform the same in most applications. Zinc oxide is used as a cure activator in the AS-NBR formula. Zinc oxide increases the vulcanization rate by activating the accelerator so that it performs more effectively.³

This change was evaluated in conjunction with the change to Agerite Stalite S®. The description of this test effort is included in the "Agerite Stalite S® Antioxidant" section below.

Agerite Stalite S® Antioxidant

Because of poor sales, the manufacturer of Agerite White® (Di-beta-naphthyl-paraphenylene diamine), an antioxidant, discontinued producing this material. Agerite Stalite S® (mixture of octylated diphenylamines) was selected as the replacement antioxidant.

Three potential replacement antioxidants were initially identified and tested by the AS-NBR supplier: Anchor DNPD (a chemically identical product), Vanox MTI (chemically different from Agerite White®), and Agerite Stalite S® (from the same family of amine antioxidants as Agerite White®). Small-scale mixing was conducted by the AS-NBR supplier. The following tests were conducted on the test batches:

- Shore A hardness
- Tensile strength and elongation
- Mooney viscosity
- Rheology

Shore A hardness, and tensile strength and elongation were repeated on cured material that was aged for 24 hours at 158 °F. The data showed no significant differences in these properties between the candidates. Agerite Stalite S® was selected based on its availability, chemical similarity, and the results from the test batches.

This antioxidant change was evaluated in conjunction with the change to Kadox® 930C noted in the previous section.⁴ Initially three full-scale 500-pound lots of AS-NBR were ordered, two evaluation lots and one control lot. The AS-NBR supplier manufactured all these lots during the same mix campaign. The following tests were conducted on the sheet stock material:

- Shore A hardness
 - Aged 2, 4, 7, 14 days, 158 °F
- Tensile strength and elongation (//, ⊥)
 - Aged 2, 4, 7, 14 days, 158 °F
- Specific gravity
- Specific heat
- Thermal conductivity
- Mooney viscosity
- Initial scorch
- Rheology
- Tear strength (//, ⊥)
- Witness panel bond tests
 - Aged 4, 16 weeks, 135 °F
- Seventy-pound charge (SPC) insulation char motors

A notable drop in initial scorch time as observed during the scorch testing of the first two evaluation lots. Initial scorch is an indication of how fast the material will begin to cross link (cure) at elevated temperatures. Two additional lots were made to evaluate the change to Agerite Stalite S® and Kadox® 903C. Each of these two lots was made using a different lot of Kadox® 930C. AS-NBR extrusions were also made from these lots to determine if the drop in initial scorch time would affect the ability to extrude the AS-NBR. SPC motor, aging, and bond tests were not repeated on these lots. Again a reduction in initial scorch time was observed.

One additional lot of AS-NBR was produced to evaluate the effects of the Agerite Stalite S® change only in an attempt to identify the cause of the shift in initial scorch. Initially it was thought that the Kadox® 930C zinc oxide, which functions as a cure activator, was the cause. Testing of this lot of material again showed short initial scorch times, indicating that the

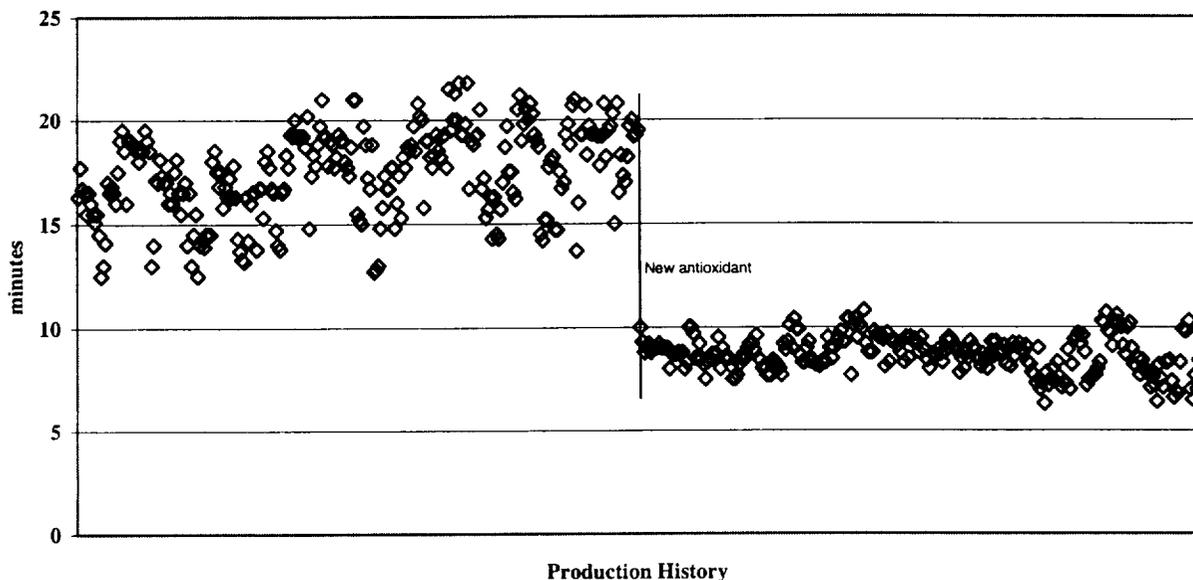
Agerite Stalite S® antioxidant was the cause of the shift in scorch time.

Six months following initial receipt and testing of the first evaluation lots, initial scorch was again tested to evaluate aging effects of the uncured material. These tests showed a typical 1-minute drop in scorch values. Rheology was also conducted and produced the same results, minimal reduction in cure initiation values.

The shift in initial scorch time was also reflected in the Ts2 data from the rheology tests. The oscillating disk rheometer essentially measures the stiffness of the rubber as the material cures. Ts2 is an indication of the time required to initiate cure, similar to initial scorch. The shift in scorch time did not affect any of the mechanical or thermal/erosion properties of the cured NBR. At the beginning of the RSRM insulated segment cure cycle, the autoclave is held at 200-230°F for approximately 2 hours. This temperature is below the curing temperature of the AS-NBR and the step is designed to provide time for all of the AS-NBR material to reach a constant elevated temperature prior to increasing the autoclave temperature to begin cure. During this hold period the AS-NBR material has time to flow into the extremities of the mold tooling. Because of this hold period, the initial scorch characteristics are less critical from a RSRM processing application standpoint. Additional scorch tests were conducted at 200°F and 230°F for 2 hours to verify that the material was not curing (at a notable rate) at these temperatures. These tests indicated that the material did not cure and would flow at these temperatures.

Initial scorch testing is retained in the AS-NBR specification because it generally gives an indication of the amount of heat history experienced by the material during mixing and processing at the manufacturer. Two RSRM igniter part cure cycles were modified to include the 200-230°F hold step. All RSRM components were successfully fabricated following implementation of the change to use Agerite Stalite S® and Kadox® 930C. The following figure illustrates the shift in scorch properties.

AS NBR - Initial Scorch Characteristics - Vendor Data
Specification Limits 5 - 30 minutes



During this evaluation it was also noted that the Agerite Stalite S® caused the AS-NBR insulation to have a lighter color before and after cure. The Agerite Stalite S® also eliminated discoloration or darkening of the cured AS-NBR caused by light exposure that had been observed prior to this change.

HiSil® 233 Silicon Dioxide

In November 1992, the AS-NBR supplier was notified of a change in the production of Hi-Sil products including Hi-Sil 233, silicon dioxide, used in AS-NBR. The alkali source used in the silica manufacturing process was changed from caustic soda to soda ash. This change was made to reduce the costs to produce their silica products.

Silica products are derived from crystalline sand (SiO₂). During the early stages of the process, the crystalline structure of the sand is broken down by converting it to high alkali glass at very high temperature. The alkali source makes the crystalline sand easier to melt (lowers the melt temperature). The alkali source is strictly a processing aid in this initial step that facilitates melting the sand in the furnace. During subsequent steps in the process, the alkali is converted to salt and eventually discarded. The silica manufacturer stated that the end silica product would not be changed with a change to the alkali source. The silica manufacturer also indicated that soda ash had been used as the alkali

source prior to 1983. No documentation of the previous change from soda ash to caustic soda was found at the AS-NBR supplier or at Thiokol.

This change affected the AS-NBR insulation and two silica filled EPDM materials used as external insulation materials for the RSRM. A test plan and test report were written to evaluate this change to both the SF-EPDM and AS-NBR insulation materials.⁵

The silica manufacturer provided physical and chemical properties data on the initial silica batches following the alkali change along with historical data for comparison. This data included surface area, pH, percent weight loss at 105° C, and purity (percent SiO₂). This data confirmed the vendor's statement that the change to the alkali source would not affect the properties of the Hi-Sil 233.

One full-scale batch of AS-NBR was produced using the new process Hi-Sil 233. Most of the batch was calendered to 0.100-inch thickness. Three AS-NBR extrusions were also made to determine if the change had any impact on the ability to extrude the AS-NBR. Both the sheet stock and extrusions were tested for the following properties:

- Shore A hardness
- Tensile strength and elongation (//, ⊥)
- Specific gravity

- Specific heat
- Thermal conductivity
- Mooney viscosity
- Initial scorch

All of the data from these tests were within specification limits and the previous historical database. Nominal test results were also obtained from the tests performed on the SF-EPDM.

Notification was received in 1994 that, due to environmental concerns, the alkali source was being changed again, back to caustic soda. Because of the conclusions drawn from the first evaluation, this change was implemented into the AS-NBR material without conducting a specific test plan. The quality conformance data from the subsequent production lots were monitored to verify that the implementation of this change did not affect AS-NBR properties.

In 1996 the silica manufacturer notified the AS-NBR supplier that a second sodium silicate furnace was being constructed. The new furnace would use soda ash as the alkali source. The original furnace would still use caustic soda. Sodium silicate from both furnaces would be blended later in the silica manufacturing process. Again this change was implemented without additional testing. The silica manufacturer also indicated that the original furnace would eventually be converted to use soda ash. The history of these silica changes indicates that the manufacturer will readily make changes to the alkali source based on market costs for these chemicals. Fortunately all of the data gathered in conjunction with changing alkali sources indicate that the alkali source has no detectable impact on the performance of AS-NBR insulation.

Harwick® F-1500 Stearic Acid

The production facility used to make Hydrofol® 1800B stearic acid (originally used in AS-NBR insulation) was purchased by a company that already had a facility to produce stearic acid. The Hydrofol® 1800B facility was closed. The AS-NBR supplier selected Harwick® F-1500 stearic acid as the replacement, based on specification properties of the two stearic acids. Harwick® F 1500 had also been used successfully to replace Hydrofol® 1800B in other insulation materials produced for Thiokol.

Stearic acid functions as a cure activator in AS-NBR. During vulcanization, stearic acid and zinc oxide react with the sulfur to increase the rate and efficiency of the cross-linking reaction.

As part of the initial test effort, Thiokol obtained samples of both Harwick® F-1500 and Hydrofol® 1800B stearic acid. The following tests were conducted to compare the two stearic acids:

- Initial and final melting point
- Ash content
- Acid number
- Saponification value
- Titre (freezing point)
- FT-IR analysis

The data from the above tests indicated that two stearic acids were very similar, providing justification to proceed with the full-scale batch mixing. The evaluation of AS-NBR made using Harwick® F-1500 stearic acid was conducted in conjunction with the evaluation of new process Picco® 6100 tackifier, and is discussed in the following section of this report.

Picco® 6100 Resin Tackifier

During the latter part of 1995, the manufacturer of Picco® 6100 resin restructured their production facility, which included shutting down old equipment and replacing it with new equipment that was more cost effective and environmentally compliant. As part of the restructuring, the resin neutralization process used to make Picco® 6100 was changed from a wet neutralization process to a dry neutralization process. The manufacturer indicated that the new process Picco® 6100 resin would meet the previous specification and perform the same as the previous material.⁶

Picco® 6100 resin is included in the AS-NBR formulation primarily to provide increased green tack of the uncured material. This is a very important property of NBR in light of the RSRM ply-to-ply insulation build process. It is also a property that is difficult to measure quantitatively.

Samples of old process and new process Picco® 6100 were obtained and the following tests were conducted to compare these two materials.

- Specific gravity
- Ash content
- Differential scanning calorimeter (DSC)
- Thermomechanical Analyzer (TMA)
- FT-IR

All of these tests indicated that the new process material would perform similar to the old process Picco® 6100 resin. Three full-scale evaluation batches were mixed to evaluate the Picco® 6100 resin change and the Harwick® F-1500 stearic acid change. These three batches were individually calendered into 0.100-inch thick sheet stock lots. Extrusions were also produced from one of these lots of AS-NBR. Two additional batches were mixed, one to evaluate only the new process Picco® 6100 resin change (with Hydrofol® 1800B stearic acid), and the other to evaluate only the Harwick® F-1500 change (with old process Picco® 6100 resin). These two additional lots were not fully tested, but were ordered so if a shift in some property was observed the specific cause (stearic acid or Picco® 6100 resin) could be identified.

The AS-NBR supplier and Thiokol conducted the qualification tests on all evaluation lots. The following additional material properties tests were conducted:

- Rheology
- Tear strength (//, ⊥)
- AS-NBR / AS-NBR T-peel
- AS-NBR / case witness panels (witness panels test both tensile and peel bond capability)
- AS-NBR / CF-EPDM witness panels
- AS-NBR / liner witness panels
- AS-NBR / carbon cloth phenolic witness panels
- AS-NBR / glass cloth phenolic witness panels
- SPC insulation char motors

Bench tests were also conducted to evaluate the tack of the uncured AS-NBR at the Chemlok® 233 vulcanization adhesive to AS-NBR interface and at the AS-NBR to AS-NBR interface. These tests were conducted using the evaluation lots and production lots of AS-NBR for comparison. Both solvent (TCA) activated samples and non-activated samples of AS-NBR were rolled against a Chemlok® 233 coated plate and against another sheet of AS-NBR. A fish scale was used to measure the peel strength required to remove the samples. Qualitative observations were also made of the tack tests.

The above noted tests verified that AS-NBR made using Harwick® F-1500 stearic acid and new process Picco® 6100 resin would perform the same as previous AS-NBR material.

Sulfur Oil

Crystex® OT 20 sulfur is used as the curative in AS-NBR insulation. Oil is added to the sulfur by the

sulfur manufacturer to prevent dusting and to improve dispersion of the sulfur during rubber mixing. Two different sources of oil had been used by the sulfur manufacturer. A new, third oil source was approved for use. The treatment oils used in Crystex® OT 20 sulfur are stored in a single holding tank. Each order of oil is added to the existing supply in the holding tank, resulting in a varying combination of the three oils. The source selected for each oil purchase is based on price and availability.

Crystex® OT 20 sulfur is mill-mixed with styrene butadiene rubber (SBR) by the AS-NBR manufacturer to make a sulfur masterbatch. The sulfur / SBR blend disperses much more readily in NBR than sulfur alone. The oil used to treat Crystex® sulfur makes up less than one quarter of one percent of the final AS-NBR insulation. Due to the similarity of the various oils used, the small amount of oil used, the presence of other hydrocarbon-derived constituents, and the presence of plasticizer, it was anticipated that the oil change would not affect the properties and performance of the AS-NBR insulation.

One batch of AS-NBR was mixed using "new oil" Crystex® sulfur. A control lot made using the same lots of raw materials (except sulfur) was tested along side the evaluation lot. Quality conformance tests were conducted by the AS-NBR supplier. Thiokol conducted all of the qualification tests along with rheology and tear strength. Bond tests, including T-peel and AS-NBR to steel witness panels, were conducted by Thiokol.⁷

The third oil source did not affect properties or performance of the AS-NBR insulation. The sulfur manufacturer has recently indicated that an additional oil source will be used in the near future. This new oil source will require another change evaluation.

Sulfur Masterbatch Refining

In November 1998 hard black spots were observed on the visible surfaces of the cured AS-NBR insulation in RSRM segments. A limited number of black hard spots are allowed in the insulated segment finalization inspection specification, but these segments had notably more than the specification allows. Analysis of extracted samples of these spots indicated that they were sulfur rich. Some of the hard spots had a yellow, pure sulfur center. Samples from the lots of the sulfur masterbatches used to make these AS-NBR lots revealed small hard Crystex® OT 20 clumps that had been compressed into small hard particles. These sulfur

particles did not break up and disperse during subsequent mixing of the AS-NBR. Further investigation determined that the SBR used to make the suspect sulfur masterbatches handled differently during mill mixing and was near the shelf life expiration date. It was also determined that the Crystex® OT 20 sulfur lot used was manufactured at a different production site than the Crystex® that had been used previously. Sulfur from the second manufacturing site had been used many years earlier.

After extensive review and additional SPC insulation char motor testing, the segments with black sulfur spots were approved for use. As corrective actions, sulfur from the second manufacturing site was no longer used, and the condition and age of the SBR were reviewed prior to mixing sulfur masterbatches.

It was also determined that a previous change of antioxidants caused the AS-NBR insulation to be lighter in color. This change caused the dark sulfur spots to visibly stand out and be more readily detectable. A review of various photos of RSRM segments that had been produced earlier revealed some dark spots on those segments.

Even with the noted corrective actions, an inspection step or processing change was desirable that would eliminate or greatly reduce the possibility of hard sulfur particles. The AS-NBR manufacturer recommended that the sulfur masterbatches be refined using a calender with a very small gap setting. This process essentially smashes all sulfur particles into thin fragile flakes that break up more readily during AS-NBR mixing.

The additional refining process was evaluated. It was determined that negligible heat was added to the masterbatch during the refining process. This change was verified by evaluating the level of insoluble sulfur in the sulfur masterbatch before and after the refining process. Insoluble sulfur or polymerized sulfur is used in AS-NBR to reduce sulfur blooming of the uncured material. Sulfur bloom can reduce the green tack of the material. By using insoluble sulfur, the sulfur particles are large enough that they are not mobile in the uncured material, reducing or eliminating sulfur bloom. During the cure cycle, the insoluble sulfur converts to soluble sulfur when heated and functions as the curative agent. A portion of the insoluble sulfur is converted to soluble sulfur during storage of the sulfur and during mill mixing of the sulfur masterbatch (due to the heat generated during the mixing process).

Samples of refined sulfur masterbatch were carefully inspected for particles. AS-NBR insulation was mixed

using refined sulfur masterbatches. These lots of AS-NBR were tested using the quality conformance tests. The AS-NBR insulation was tested in SPC insulation char motors. Large sheets of the calendered AS-NBR were cured and inspected for black hard spots. These inspections indicated that the addition of the sulfur masterbatch refining step greatly reduced the size and number of black spots in the cured AS-NBR.

Sulfur Masterbatch Crossblending

In an effort to reduce testing costs and to reduce variation in sulfur masterbatches, a crossblending step was added to the sulfur masterbatch manufacturing process. Crossblending entails mill mixing three 50-pound sulfur masterbatches into a 150-pound crossblended masterbatch. Each crossblended batch is then sampled for sulfur analysis (percent total sulfur and percent insoluble sulfur). Previously each 50-pound sulfur masterbatch was sampled and tested by an outside laboratory.

Crossblending of batches is a practice used in the manufacturing of most RSRM insulation materials. Crossblending reduces batch-to-batch variation of these products. It also reduces testing, documentation, and packaging costs. The primary purpose for crossblending is to produce a more homogenous product.

This change was evaluated primarily by testing sulfur masterbatches. Six 50-pound sulfur masterbatches were produced. Each of these six masterbatches was sampled for sulfur analysis. Groups of three masterbatches were then mill-mixed into two crossblended sulfur masterbatches. These crossblended masterbatches were then sampled. The crossblended sulfur masterbatches were again sampled following the refining step (discussed earlier in this report). The insoluble sulfur contents were compared to determine if any noticeable degree of additional heat history had been experienced by the sulfur masterbatch.

The insoluble sulfur levels of the evaluation batches indicated that the crossblending process did not affect the sulfur masterbatch (and decrease the insoluble sulfur levels). The products were then used to mix a full-scale lot of AS-NBR. The specification quality conformance data were reviewed and found to be within specification limits and recent historical data.

Conclusion

The methodology used in evaluating raw material changes to RSRM elastomeric insulation materials has proven effective. The performance of AS-NBR has not changed despite the numerous obsolescence issues that have occurred. A similar change evaluation approach should be used for future changes, using the test methods available and any appropriate new test technologies.

References

- 1) Robert O. Babbit, The Vanderbilt Rubber Handbook, R.T. Vanderbilt Company, Inc., Norwalk, CT, 1978.
- 2) D. G. Guillot, H. Feldman, Report on Test Plan ETP-0045 Evaluation of New Altax® and Captax® Accelerators in NBR and EPDM SRM Elastomeric Insulation Material, TWR-17281, Morton Thiokol Publication, October 1987.
- 3) Maurice Morton, Rubber Technology, Van Nostrand Reinhold Company, New York, 1987.
- 4) S. D. Mildenhall, Test Report NBR Antioxidant and Activator Evaluation, TWR-61790 (Test Plan WTP-0270), Thiokol Corporation Publication, June 1993.
- 5) S. D. Mildenhall, Test Report Evaluation of New Process Hi-Sil 233 in Asbestos Silica-Filled NBR, DL-1375, and O53A Silica-Filled EPDM Insulations, TWR-64554 (Test Plan ETP-1158), Thiokol Corporation Publication, June 1993.
- 6) S. D. Mildenhall, Final Test Report for ETP-1488 Evaluation of Harwick® F-1500 Stearic Acid & New Process Picco® 6100 Resin, TWR-73559, Thiokol Corporation Publication, April 1997.
- 7) F. B. Baugh, Final Test Report for ETP-1766 Evaluation of a Third Oil Source for NBR, TWR-76042, Thiokol Propulsion Publication, March 1999.